Rühl et al. [109] reported on the content of volatile nitrosamines in the mainstream and sidestream smoke of German commercial cigarettes. The values provided are between 1.8 and 13.8 ng per cigarette for dimethylnitrosamine in the mainstream smoke and between 213 and 558 ng for the sidestream smoke. The corresponding values for pyrrolidinenitrosamine are 3.1-30.3 ng per cigarette in the mainstream smoke and 296-700 ng per cigarette for the sidestream smoke.

The dimethylnitrosamine concentration was also determined by Stehlik et al. [125] in the air of smoke-filled rooms. The amounts of nitrosamine found under ordinary living and working conditions are between 0.01 and 0.07 ng per liter of air. 0.15 ng, for example, was found during a test which is to be considered as an extreme situation. Here 38 cigarettes were smoked by three persons within a period of two hours in a 22-$m^3$ conference room. The windows and doors were closed throughout the entire test period. The authors found that after only 20 mins from the start of the test the people present complained of burning in the eyes and bad air. At the end of the test, nausea and headaches were reported by the test persons. Thus Weber's statement is confirmed, i.e., that the loading of a 30-$m^3$ room with the sidestream smoke from five cigarettes leads to an impairment in the feeling of well-being of the persons in the room [134].

When the dimethylnitrosamine loading of the air in interior rooms found by Stehlik et al. [125] is compared with the data found by Hoffmann's group for the nitrosamine concentration in bars, lounges, etc. [13], it can be seen that Stehlik finds much lower values. Peak values such as 0.24 ng dimethylnitrosamine per liter of air as found the Hoffmann group in a bar is not even remotely approached by Stehlik. A high loading of this magnitude could be reached according to his results only if one cigarette were to be smoked per cubic meter of room [124]. Under these smoke density conditions, however, it would be impossible to stay in such rooms for any extended period.

Data on tobacco-specific nonvolatile nitrosamines of the tobacco alkaloids in mainstream and sidestream smoke are also supplied by Hoffmann's group [44]. The separation of the alkaloid nitrosamines was carried out by Hoffmann by means of high-performance liquid chromatography; detection was again carried out by means of the substance-specific TEA. In the mainstream and sidestream smoke, *N*-nitrosonornicotine, *N*-nitrosoanatabine, and 4-(*N*-methyl-*N*-nitrosoamino)-1-(3--pyridyl)-1-butanone were found. The measurement values obtained are given in Table 32.

Table 32.

An additional publication on this group of compounds was recently published by Piade, Adams, and Hoffmann [99].

On comparison of the analytical results of tobacco-specific nitrosamines with those of volatile nitrosamines in tobacco smoke, it is seen that the alkaloid nitrosamines occur primarily in the mainstream smoke. This is the case for nitrosoanatabine in all the cigarettes tested; for nitrosonornicotine, the tobacco mixture seems to have a strong influence.

4-(*N*-methyl-*N*-nitrosoamine)-1-(3-pyridyl)-1-butanone, however, is present in greater amounts in the sidestream smoke than in the mainstream smoke. No explanation of these differences in the distribution of volatile and nonvolatile nitrosamines between the two smoke streams is provided by Hoffmann.

Hoffmann et al. found 43 ng of *N*-nitrosodiethanolamine in the sidestream smoke of a nonfilter 85-mm cigarette; in the mainstream smoke of this cigarette, they detected 36 ng [45]. The SS/MS ratio is therefore 1.19. It must be pointed out, however, that this nitrosamine is to be found only in the smoke of

cigarettes whose tobacco was treated with the suckering control agent maleic hydrazide-diethanolamine.

## 10. Hydrocarbons

Johnson et al. [55] determined methane, acetylene, and propane/propene by means of gas chromatography in the mainstream and sidestream smoke of experimental cigarettes (Table 33).

Table 33.

The same group of authors report on the occurrence of toluene in sidestream smoke (Table 34).

Table 34.

Jermini et al. [53] studied the content of the sidestream smoke of a 100-mm long U.S.-blend filter cigarette to determine lower aromatic hydrocarbons. The cigarettes were smoked in a 30-$m^3$ room. The values found are given in Table 35.

Table 35.

The distribution of distillable alkanes between the mainstream and sidestream smoke depends on their molar weight and thus on their boiling point [4]. Hale et al. [33] studied the transfer of a series of saturated, standard hydrocarbons into the mainstream and sidestream smoke of cigarettes. The alkanes used by them extended from *n*-decane to *n*-decosane. They reported that hydrocarbons with lower molecular weights are carried over mainly into the sidestream smoke.

Boyd and Craig [6] determined the distribution of a similar series of alkanes between the two smoke streams and came to the opposite result. Their results agree, however, with a mathematical model developed by them for the distillation processes in the burning cigarette.

## 11. Other Gas-Phase Components

Johnson [55] also provides data on the distribution of methyl furan and methyl chloride between the sidestream and mainstream smoke (Table 36). With regard to the methyl furan, no distinction was made between the 2- and the 3-methyl isomers.

Table 36.

## 12. Phenols

The first data on the phenol distribution between mainstream and sidestream smoke are to be found in Neurath [83]. After nonfilter 80-mm German-blend cigarettes were smoked, he found 228 μg of phenol in the mainstream smoke and 603 μg in the sidestream smoke. This gives a SS/MS ratio of 2.64. The phenol determination was carried out by Neurath by means of the color reaction with 4-aminoantipyrine [77]. This method includes most of the steam-volatile phenols with free ortho- and para- positions with respect to the hydroxyl group.

Brunnemann, Lee, and Hoffmann also found 212 μg of pyrocatechol in the sidestream smoke of nonfilter, 85-mm U.S.-blend cigarettes [11]. In the mainstream smoke of this cigarette, 272 μg were found, which results in a SS/MS ratio of 0.78. The corresponding values for the 85-mm U.S. filter cigarette are 88 μg and 136 μg, for a ratio of 0.65. In contrast to the steam-volatile phenols,

pyrocatechol and its alkyl derivatives are not selectively retained by cellulose acetate filters from the mainstream smoke. Because the SS/MS ratio for steam-volatile total phenols is greater than two, the authors assume that pyrocatechol is formed during smoking by a different mechanism or from other precursors than that responsible for the monophenols.

Cornell, Cartwright, and Olender reported in 1978 on the distribution of 14 volatile phenols between the mainstream and sidestream smoke of cogarettes and cigars [23]. Phenol, guaiacol, the cresol isomers, ethylphenol isomers, and the dimethylphenols were included. According to the data of this group, the phenol distribution in the smoke streams of cigarettes and in small and medium cigars corresponds to the amount of tobacco smoked. In large cigars, the phenols are concentrated especially in the sidestream smoke. The following sidestream-mainstream smoke distributions were found:

| | |
|---|---|
| phenol: | 3-105; |
| cresol isomers: | 1-20; |
| guaiacol: | 1-14; |
| ethylphenol isomers: | 1-10; and |
| dimethylphenol isomers: | 0.5-21. |

According to this group of authors, a total of 23-263 μg of this group of compounds occurs in the mainstream smoke of the tested smoke products and 269--1,157 μg in the sidestream smoke.

Harris and Hayens determined the phenol distribution between the two smoke streams by means of the sidestream smoke apparatus developed by them for a large group of different commercial cigarettes [37]. The SS/MS ratios found by them are between 1.7 and 3.6 for nonfilter and 9.1-20.0 for filter cigarettes. The ratios for the filter cigarettes, which are extremely high in some cases, are

caused by the selective effect of cellulose acetate filters on this group of compounds and by ventilation filters.

### 13. Polycyclic Hydrocarbons

As early as 1960, Pyriki, Müller, and Moldenhauer reported that benzo[a]-pyrene occurs in the sidestream smoke of cigarettes in higher concentrations than in the mainstream smoke [106, 197, 198]. The authors smoked the cigarettes according to the conditions proposed by the PFYL [97]; the smoking apparatus corresponds to that developed by Wahl and Heil [131]. The sidestream smoke rising from the burning end was collected in a bell. On the basis of the cigarettes tested, Pyriki found that on average, the benzo[a]pyrene content of the sidestream smoke was twice as high as that of the mainstream smoke. In addition to benzo[a]pyrene, Pyriki also determined the distribution of 1,2-benzanthracene, pyrene, and phenanthrene. The results he found are reproduced in Table 37.

Table 37.

Because of the smoking conditions (puff volume, puff length, smoking machine, etc.) chosen by the authors, these analytical results are comparable with the more recent results of other research groups to only a limited extent.

The first values obtained with the smoking procedures standard today were published by Neurath et al [83]. He found 38 ng of benzo[a]pyrene in the mainstream smoke and 131 ng in the sidestream smoke. The SS/MS ratio resulting from this of 3.5 confirms Pyriki's findings that this compound occurs in a greater concentration in the sidestream smoke than in the mainstream smoke.

Schmeltz, Tosk, and Hoffmann [113] report on the occurrence of naphthaline

and its alkyl derivatives in cigarette smoke. The values found by this research group in an 85-mm-long nonfilter, American-blend cigarette are summarized in the following table.

Table 38.

The naphthalines thus occur in clearly higher concentrations in the side-stream smoke in comparison with the mainstream smoke than does, for example, benzo[a]pyrene. The authors do not provide an explanation for this finding.

For pyrene, Kotin and Falk give a SS/MS ratio of 3.0 [72].

Aza analogs of polycyclic hydrocarbons in the mainstream and sidestream streams of cigarettes and cigars were determined by Dong et al. [27]. The values found by this group for a nonfilter, 85-mm-long U.S.-blend cigarette are shown in Table 39.

Table 39.

The authors also state that the SS/MS ratio for quinoline in cigars is clearly higher than in cigarettes and is between 30 and 90.

Harmanne and norharmane were detected as early as 1962 by Pointexter and Carpenter in the mainstream smoke of cigarettes [100].

The distribution of these compounds between the mainstream and sidestream smoke of the German uniform cigarette E-76 (84-mm-long filter cigarette), a dark cigarette, and a series of experimental cigarettes was studied by Neurath [88].

The values were obtained by means of high-pressure liquid chromatography (UV detector, adsorption at 347 nm). The analytical results were confirmed by the combination of gas chromatography and mass spectrometry. The results are shown in Table 40.

Table 40.

For harmane, the values of the blend, the Virginia-Oriental, and the Burley cigarettes in the mainstream smoke are between 1.1 and 3.1 μg; for norharmane, they are between 3.2 and 7.1 μg. The mainstream smoke values for the cigarettes of Burley ribs are clearly lower (0.2-0.9 μg). The cigarettes made of strip tobacco (paper process) also tend to have lower values.

The concentration of these two carbolines (blend cigarettes and cigarettes on only one tobacco type) are generally higher in the sidestream smoke (2.1-3.5 μg harmane and 11.0-13.9 μg norharmane). This study confirms the view already expressed earlier by Neurath that pyrolytically formed compounds occur in higher concentrations in the sidestream smoke than in the mainstream smoke [87].

Schmeltz et al. [111] and Brunnemann et al. [16] share this view.

## 14. Steroids

Schmeltz, DePaolis, and Hoffmann determined the distribution of several steroids between sidestream and mainstream smoke [112]. The tested cigarettes were again the 85-mm-long American-blend cigarettes. The ratios found for the individual compounds are summarized below.

| | SS/MS |
|---|---|
| cholesterol | 0.8; |
| campesterol | 0.9; |
| stigmasterol | 0.8; and |
| β-sitosterol | 0.8. |

## 15. Heavy Metals

According to Petering, the sidestream/mainstream smoke ratio for cadmium is 3.6 [96]. This finding was confirmed by Hay [38].

In an article by a research group under Petering [Menden et al.], the distribution of the heavy metals cadmium, nickel, zinc, and lead was described for the mainstream smoke, sidestream smoke, butts, and ashes of cigarettes [78]. The cigarettes tested were nonfilter Kentucky 1R1 Reference Cigarettes, and a nonfilter 85-mm commercial cigarette was also studied. The determination of the heavy metals was carried out by means of atomic absorption spectroscopy. The concentration of these metals in the sidestream smoke was not determined directly, but rather calculated by means of the quantitative balance (micrograms of metal in the tobacco minus the amount detected in the mainstream smoke, ashes, and butt). Table 41 shows the values published by this group.

Table 41.

In order to confirm the calculated cadmium content of the sidestream smoke, the authors point out that in a preliminary experiment in which the sidestream smoke was collected directly, a value was found whose order of magnitude was similar to that of the estimated value [41].

With regard to lead, the authors state that most of this metal remains behind in the ash. The transfer rate from tobacco to mainstream smoke is said to be only 1.8-1.9%. It appears unlikely to them that the sidestream smoke could contain any significant amount of this metal.

With regard to the heavy metal concentrations given by Menden for mainstream smoke, it should be remarked that only the amount occurring in the particle phase

was determined by this group. The gas phase was not considered. A slight shift in the calculated SS/MS ratio in favor of the mainstream smoke would be possible.

Szadkowski et al. [127] give a value for the cadmium content of the sidestream smoke which is on the same order of magnitude as that given by Menden [78].

Sunderman and Sunderman dealt as early as 1961 with the distribution of the nickel present in tobacco as the tobacco is smoked [126]. The data found by them are shown in Table 42. The concentration in the sidestream smoke was again calculated by way of a quantitative balance.

Table 42.

Without proof, Sunderman and Sunderman assumed on the basis of the reactivity of very finely divided nickel with carbon monoxide that this metal is present in the tobacco smoke essentially in the form of nickel tetracarbonyl. Pailer and Kuhn [93] point this out in their article on the nickel content of cigarette smoke. They established that nickel carbonyl decomposes at 180-200°C into carbon monoxide and metallic nickel. It can therefore be expected that any nickel tetracarbonyl possibly formed in the mainstream smoke would decompose as soon as it reaches the lower temperature regions behind the glow zone. They could neither confirm nor fully exclude the occurrence of nickel carbonyl.

As a footnote to Sunderman's article it can be remarked that it cannot be derived directly from the article with any accuracy how the cigarettes tested were smoked. It is mentioned that work was carried out with an intermittent vacuum and at a flow rate of 225 ml per minute per cigarette. But no mention is made of the puff volume or of the puff frequency. These smoking parameters, however, are of crucial importance both for the qualitative and especially for the

quantitative composition of the smoke. This is therefore an explanation for the fact that the mainstream smoke values (0.37 and 0.58 μg of nickel per cigarette) found by these authors are about a power of ten higher than those given by other research groups (e.g., Menden et al.: 0.02 and 0.08 μg Ni/cigarette [78]; Pailer and Kuhn: 0.06 μg Ni/cigarette [93]; Perinelli and Carugno: 0.004-0.005 μg Ni/ /cigarette [95].

Szadkowsky and Schultze [127] also studied the nickel content of sidestream smoke. They give the maximum possible nickel concentrations in the air caused by cigarette smoke as 14 $\mu g/m^3$. This corresponds to a nickel-tetracarbonyl concentration of 42.5 $\mu g/m^3$. This value is considerably below the MAC concentration for this compound valid since 1979 in the Federal Republic of Germany (MAC value: 700 μg $Ni(CO)_4/m^3$).

## IV. CONCLUDING REMARKS

The question as to the exposure or risk of the nonsmoker resulting from sidestream smoke is discussed in detail in "Smoking and Health, A Report of the Surgeon General, U.S. Department of Health, Education, and Welfare, 1979" [122].

In this context, an attempt is made to evaluate the substances detected in sidestream smoke. The qualitative differences in the composition of mainstream and sidestream smoke are treated. The following opinion is expressed, which can stand as the conclusion of this review:

"The actual account of the substance and the mainstream to sidestream ratio will vary with different types of tobacco tested and the method used to burn the cigarette . . . Many of the substances, including nicotine, carbonmonoxide and ammoniac are found in much higher concentrations in the sidestream smoke than in the mainstream smoke. Thus, the total smoke exposure of nonsmokers is

quantitatively much smaller than the exposure of smokers, but the smoke nonsmokers inhale may be quantitatively richer in certain compounds than mainstream smoke. This qualitative difference in smoke exposure makes the quantification of the involuntary smoking in terms of "cigarette equivalents" confusing and inaccurate. It requires that involuntary smoking be evaluated as a separate problem not subject to simple extrapolation of an understanding of dose-response relationship of cigarette smoking."

The statement by the Surgeon General of the United States clearly shows the problems of evaluating the quantitative values summarized in this article for the mainstream and sidestream smoke with regard to the possible health risks of nonsmokers. It is also a standard against which articles such as those by Orlien could be measured [90]. Orlien attempts to estimate the concentration of these substances in the sidestream smoke on the basis of known quantitative data for various compounds in the mainstream smoke and to derive from this the degree of health risk to which nonsmokers are exposed. Aside from the fact that his estimates do not agree in some cases with the actual measurement results, this procedure contradicts the criteria cited above and tends more to confuse than to clarify the issue of "passive smoking".

LIST OF THE TABLES APPEARING IN THE ARTICLE

Table 14. Molecular nitrogen and ammonia in the sidestream smoke of cigarettes smoked in a $He-O_2$ atmosphere [56].

Table 15. Ratio of $^{15}N^{15}N$ to $^{15}N^{14}N$ in the molecular nitrogen and ammonia of the sidestream smoke of experimental cigarettes after smoking in a $He-O_2$ atmosphere (80:20) [56].

Table 16. Distribution of nitriles between mainstream (MS) and sidestream (SS) smoke [55].

Table 17. Distribution of hydrocyanic acid between mainstream (MS) and sidestream (SS) smoke of cigarettes [14].

Table 18. Distribution of hydrocyanic acid between mainstream (MS) and sidestream (SS) smoke of cigars [14].

Table 19. Nitriles in the sidestream smoke of a 100-mm, U.S.-blend filter cigarette [43].

Table 20. Ammonia distribution between mainstream (MS) and sidestream (SS) smoke of 85-mm nonfilter cigarettes [55].

Table 21. Distribution of ammonia between mainstream (MS) and sidestream (SS) smoke of cigarettes and cigars [10].

Table 22. Aromatic amines in the mainstream (MS) and sidestream (SS) smoke of a 70-mm nonfilter U.S.-blend cigarette [94].

Table 23. Pyridine distribution between mainstream (MS) and sidestream (SS) smoke of 85-mm nonfilter cigarettes [55].

Table 24. Distribution of volatile, aromatic nitrogen bases between mainstream (MS) and sidestream (SS) smoke [16].

Table 25. Effect of the air flow rate through the modified Neurath chamber on the NO content of the cigarette smoke [30].

Table 26. Volatile nitrosamines in the mainstream (MS) and sidestream (SS) smoke of cigarettes [13].

Table 27. Volatile nitrosamines in the mainstream (MS) and sidestream (SS) smoke of Swiss commercial cigarettes [17].

Table 28. Volatile nitrosamines in the mainstream (MS) and sidestream (SS) smoke of German commercial cigarettes [17].

Table 29. Dimethylnitrosamine concentration is an experimental 20.87-$m^3$ chamber after the machine-smoking of cigarettes [124].

Table 30. Nitrosamine content of the sidestream smoke of various cigarettes [124].

Table 31. Nitrosamine concentration in the air of a hermetically sealed chamber as a function of the number of cigarettes smoked [124].

Table 32. Distribution of the alkaloid nitrosamines between mainstream (MS) and sidestream (SS) smoke [44].

Table 33. Sidestream (SS)/mainstream (MS) ratio of lower hydrocarbons in the smoke of experimental cigarettes (85-mm nonfilter) [55].

Table 34. Sidestream (SS)/mainstream (MS) ratio of toluene in the smoke of experimental cigarettes (85-mm, nonfilter) [55].

Table 35. Lower aromatic hydrocarbons in the sidestream smoke of a 100-mm-long, U.S.-blend filter cigarette [53].

Table 36. Distribution of methyl chloride and methyl furan between side-stream (SS) and mainstream (MS) smoke of experimental cigarettes (85 mm, non-filter) [55].

Table 37. Polycyclic hydrocarbons in mainstream (MS) and sidestream (SS) smoke [106, 197, 108].

Table 38. Naphthalines in the mainstream (MS) and sidestream (SS) smoke of a 85-mm, U.S.-blend commercial cigarette [113].

Table 39. Quinolines and aza-polycylic compounds in the mainstream (MS) and sidestream (SS) smoke of a nonfilter, 85-mm, U.S.-blend cigarette [27].

## LIST OF FIGURES

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